Graphene *via* molecule assisted ultrasound induced liquid-phase exfoliation: A supramolecular approach

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Abstract

Graphene is a two-dimensional (2D) material holding unique optical, mechanical, thermal and electrical properties. The combination of these exceptional characteristics makes graphene an ideal model system for fundamental physical and chemical studies as well as technologically ground breaking material for a large range of applications. Graphene can be produced either following a *bottom-up* or *top-down* method. The former is based on the formation of covalent networks suitably engineered molecular building blocks undergoing chemical reaction. The latter takes place through the exfoliation of bulk graphite into individual graphene sheets. Among them, ultrasound-induced liquid-phase exfoliation (UILPE), is an appealing method, being very versatile and applicable to different environments and on various substrate types. In this book chapter, we describe the recently reported methods to produce graphene *via* molecule-assisted UILPE of graphite aiming at the generation of high quality graphene. In particular, we will focus on the supramolecular approach, which consists in the use of suitably designed organic molecules during the UILPE of graphite. These molecules act as graphene dispersion-stabilizing agents during the exfoliation. This method relying on the joint effect of a solvent and *ad-hoc* molecules to foster the exfoliation of graphite into graphene in liquid environment represents a promising and modular method towards the improvement of the process of UILPE in terms of the concentration and quality of the exfoliated material. Furthermore, exfoliations in aqueous and organic solutions are presented and discussed separately.

1. Introduction

Graphene, a 2D honeycomb lattice of carbon atoms, has emerged as a fantastic material possessing outstanding electrical, optical, mechanical, and thermal properties.[1] In view of its superior characteristics, this *wonder* material holds potential to influence future emerging technologies, including solar cells,[2, 3] light-emitting devices,[4] photodetectors,[5, 6, 7, 8] touch screens,[9] spin valves,[10, 11] ultrafast lasers,[12, 13] and flexible and wearable electronics,[14] to name a few. Moreover, its surface area, quantified experimentally being as high as 2700 $m^2 g^{-1}$,[15, 16] have made graphene an attractive system for gas,[17, 18, 19] and energy[15, 20, 21] storage, (micro-) optoelectronics,[22, 23, 24, 25] catalysis,[26, 27] energy conversion,[15] as well as in biological labelling.[28]

Graphene can be produced and isolated either following the *bottom-up* or the *top-down* strategy.[29, 30] Graphene can be obtained in very high quality sheets by exploiting the *bottom-up* covalent association of small molecular building blocks, undergoing chemical reaction to form 2D networks[31, 32, 33]; however, the quantity of materials produced with this method is limited. The growth on (catalytically active) solid surfaces achieved by chemical vapour deposition (CVD),[34, 35] or *via* silicon evaporation from silicon carbide,[36] represent alternative *bottom-up* paths. *Top-down* approaches, which are based on the separation of graphene sheets from graphite, can be carried out under various environmental conditions.[37, 38] In particular, defect-free sheets can be obtained by making use of the micromechanical cleavage,[39] and microwaves.[40] Amongst the *top-down* methods, liquid-phase exfoliation (LPE), which can be further divided in the three sub-methods, i.e. ultrasound-induced LPE (UILPE),[41, 42, 43, 44, 45, 46, 47] electrochemical exfoliation (EE),[48, 49, 50, 51, 52] high-shear mixing (HSM),[53, 54] and is an attractive approach, being extremely versatile and applicable to various experimental conditions. Whereas *bottom-up* approaches, and in particular CVD, can yield large size graphene, LPE gives limited sheet sizes.[43, 55, 56, 57] Nonetheless, LPE has numerous advantages. It is a

viable inexpensive process that can be easily up-scaled to mass-produced dispersions processable by well-established methods, like spin-coating, drop-casting, screen-printing and ink-jet printing.[58, 59, 60] High-yield exfoliation and dispersion of graphene in high quantities into the liquid phase is key for fundamental studies and for practical applications.[14] Hence, increasing research efforts are being dedicated to the production of graphene *via* LPE, and especially *via* UILPE and to improve the material's physicochemical and electrical properties. Remarkably, the versatility of the UILPE enables the exploration of various 2D layered systems,[41, 42, 61, 62] like transition metal dichalcogenides (TMDs) exhibiting different composition, e.g. MoS_2, WS_2, $NbSe_2$, TaS_2, as well as graphene-like (hexagonal) structures like *h*-BN,[63] thereby making it possible to modulate various physico-chemical properties of 2D materials.

In this *Chapter*, we highlight the recent advances in the field of production of high quality graphene by means of UILPE of graphite. In particular, we discuss the mechanisms of exfoliation and methods that are used to characterize graphene. We then discuss numerous UILPE examples by sub-dividing them into two major classes, i.e. molecule-free and molecule-assisted UILPE. Moreover, exfoliation in aqueous and organic solutions is discussed separately.

2. Ultrasound-induced liquid-phase exfoliation

The effective exfoliation of graphite towards graphene requires the overcoming of the van der Waals attractions between the adjacent sheets. An efficient and straightforward method to lower the strength of the van der Waals interactions is the liquid immersion. Although the van der Waals interactions between adjacent sheets are weak enough to let them slide on each other in the direction perpendicular to the *c*-axis, the interactions are strong enough to inhibit the exfoliation of graphite into individual graphene sheets. This issue can be overcome by making use of external physical forces to the graphite immersed in the solvent.

In particular, graphite can be exfoliated in liquid environments by using ultrasounds to extract individual layers.[12, 43, 45, 55, 56, 64, 65, 66, 67]

Figure 1. HERE

After the exfoliation, the solvent-graphene interaction needs to balance the inter-sheet attractive forces. Solvents with surface tension (γ) ~ 40 mJ m^{-2},[45] have been found being ideal for dispersing graphene and graphitic flakes, since they minimize the interfacial tension between the graphene and the solvent, e.g. N-Methyl-2-pyrrolidone (NMP; γ - 40 mJ m^{-2}), N,N-Dimethylformamide (DMF; γ - 37.1 mJ m^{-2}), *ortho*-dichlorobenzene (*o*-DCB; γ - 37 mJ m^{-2}).[45] Despite extensive efforts in this field, the UILPE of pristine graphite can be achieved in a limited number of solvents. The use of these solvents has some downsides that cannot be overlooked, e.g. NMP and *o*-DCB can cause irritation of the eyes and respiratory tract. Furthermore NMP and DMF are toxic for multiple organs.[68, 69] Therefore, the search of alternative solvents for graphene exfoliation has gathered considerable attention in the past few years.

In 2009 Bourlinos[70] and collaborators studied the efficiency of peculiar class of fluorinated solvents. In particular, perfluorinated analogous of hydrocarbon solvents, i.e. benzene, toluene, nitrobenzene, and pyridine, have been used. The performance of each solvent was reported as follows: octafluorotoluene ~ pentafluoropyridine < hexafluorobenzene < penta fluorobenzonitrile. Depending on the solvent, the concentrations of the graphene dispersions, mostly composed of few-layered graphene, ranged between 0.05 and 0.1 mg mL^{-1}.

Recently, Sun[71] and collaborators have shown that graphene can be efficiently dispersed in amine-based solvents, namely 3,3'-iminobis(*N,N*-dimethylpropylamine) (DMPA), *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMA), 2-(tert-butylamino)ethyl

methacrylate (BAEMA) and 2-(dimethylamino)ethyl methacrylate (MAEMA). Albeit the concentration of graphene dispersions was found as high as 15 mg mL^{-1} (estimated *via* analysis of absorption coefficient), no information on the sheet(s) thickness was provided.

The comparison of values of graphene concentration obtained in the different labs and using different methods is one of the hottest matters in the field. The concentration of graphene as well as the lateral flake size varies considerably from one article to another. This can be due to the fact that (slightly) dissimilar experimental conditions, like initial graphite concentration, sonication power, solvent volume and temperature employed by numerous groups, are (with a few exceptions) commonly not indicated or not discussed. Thus, it is of fundamental importance to define a reproducible procedure relying on the best experimental conditions for LPE and in particular for UILPE, as well as the exploits defined standards for describing the graphene dispersions. In particular, the yield of LPE is defined as the ratio between the weight of dispersed graphitic materials and that of the starting graphite flakes (Y_W [%]).[29] The yield by single-layered graphene (Y_S [%]), is defined as the ratio between the number of SLG and the total number of graphitic flakes in the dispersion. The yield by SLG weight (Y_{WS} [%]) is expressed as the ratio between the total mass of dispersed SLG and the total mass of all dispersed flakes. The Y_W does not provide information on the quantity of SLG, but only on the total amount of graphitic material. Yields by Y_S and Y_{WS} are more appropriate to quantify the amount of dispersed SLG sheets.

Various characterization techniques must be employed in parallel if one wants to perform a thorough qualitative and quantitative analysis of the exfoliated material. In particular, quantitative information can be evaluated by providing the yield of exfoliation expressed in terms of Y_W, the qualitative analysis provides more relevant details such as the Y_S or Y_{SW}, the lateral size of the flakes and the presence/absence of defects. Presently, the only reliable method to identify the number of graphene layers (*N*) in material produced by UILPE is high-resolution transmission electron microscopy (HR-TEM).[56] Together with

the information coming from electron diffraction patterns, in HR-TEM the number of layers can be directly counted by analysing the sheet edges.[72] The *N* can be also quantified by exploiting atomic force microscopy (AFM) imaging. However, it is worth noting that SLG height *via* AFM depends on the substrate and on the environmental conditions, e.g. relative humidity. Actually, on mica SLG thickness amounts to ~ 0.4 nm[73] while on SiO_2 SLG appears to have a height of ~1 nm.[39] Raman spectroscopy allows identification of structural damages, electronic perturbations, as well as non-covalent functionalization and chemical modifications (possibly) occurring during the UILPE, processing or deposition of graphene on various substrates.[74, 75] The analysis of Raman spectra can give insight into the number and position of broken-conjugation areas in graphene, known as graphene atomic- or point-defects, which can influence the electronic properties of graphene. Over the past years, there has been a major step towards the understanding of Raman spectroscopy of graphene, powered by new results on doping,[76, 77, 78] edge defects,[79, 80, 81] electrical mobility[82, 83] and oxidation.[84]

2. Molecule-assisted UILPE

The use of properly selected organic molecules can enhance the exfoliation of bulk graphite into graphene, in particular when the molecules have a high energy of adsorption on the basal plane of graphene. These molecules, mainly act as graphene dispersion-stabilizing agents (DSAs) interacting non-covalently with graphene, i.e. through the physisorption of their hydrophobic tails on the graphene surface during the process of exfoliation of graphite *via* UILPE.

2.1. Dispersions in aqueous solutions

Water, the ”natural” solvent, has γ ~72 mJ m^{-2},[85] being too high for dispersing graphene and graphite,[86] because of the hydrophobic nature of graphene sheets.

Nevertheless, the use of water as a liquid medium in UILPE of graphite is of interest for the use of graphene as component in biocompatible materials.[87, 88] Remarkably, the low performance in UILPE when water is used as media can be overcome by employing DSAs molecules, to help the exfoliated graphene sheets to remain dispersed, and hinder their aggregation.[89, 90, 91, 92, 93, 94, 95, 96, 97]

Among DSAs, polycyclic aromatic hydrocarbons (PAHs)[98, 99, 100, 101] substituted with various side groups are the most studied compounds.[102, 103] Adsorption of PAHs onto the graphene surface takes place *via* π−π interactions between the planar π-conjugated surfaces. In these non-covalent interactions both PAHs and graphene aromatic planar surfaces share the electrons of π-orbitals, which ultimately results in the reduction of the surface free energy of the dispersion.

In the past decades, pyrene derivatives have been successfully employed to stabilize CNTs dispersions,[104] and as in the case of NMP, they have been adopted for UILPE of graphite.[105, 106, 107, 108, 109, 110, 111, 112, 113] Noteworthy, DSAs suitable for dispersing CNTs with a curved surface may not always be adapt for dispersing graphene, which features a flat surface. Figure 2 depicts the chemical formulae of different polycyclic aromatic hydrocarbons (PAHs) derivatives employed as the DSAs.

Figure 2. HERE

In particular, in 2010 He and co-workers[113] dispersed SLG into an aqueous dispersion by using 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt ($Py(SO_3)_4$) and aminomethylpyrene ($PyMeNH_2$) as DSAs, and fabricated transparent conductive films. Yet, neither the yield nor the effectiveness of the protocol was discussed. In 2012, a number of pyrenes were utilized by

Green and co-workers[110] to test their performance as DSAs. Among all investigated pyrenes, i.e. Pyrene (Py), 1-Pyrenecarboxylic acid (PyCA), 1-Pyrenebutyric acid (PyBA), 1-Pyrenesulfonic acid hydrate (PySAH), 1-Aminopyrene ($PyNH_2$), 1-Aminomethyl pyrene ($PyMeNH_2$), 1-Pyrenebutanol (PyBOH), 1-Pyrenesulfonic acid sodium salt ($PySO_3$) and 1,3,6,8-Pyrenetetrasulfonic tetra acid tetra sodium salt ($Py(SO_3)_4$), the $PySO_3$ was found being the most efficient, yielding graphene dispersion concentration as high as 1 mg mL^{-1}. To quantify the amount of SLG and FLG in the dispersions, the $PySO_3$-stabilized graphene samples were characterized by HRTEM, which revealed the presence of 2-4 layers thick sheets, as commonly observed in UILPE samples.

Recently Palermo and collaborators[108] went one step further and explored the thermodynamics of molecule-assisted UILPE of graphite. The authors investigated the mechanism of physisorption of different pyrenes on the surface of graphene, and successive UILPE in water. An in-depth analysis was carried out on pyrenes functionalized with sulfonic groups. In particular 1-Pyrenesulfonic acid sodium salt ($PySO_3$), 6,8-Dihydroxy-1,3-pyrenedisulfonic acid disodium salt ($Py(OH)_2(SO_3)_2$), 8-Hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt ($PyOH(SO_3)_3$), and 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt ($Py(SO_3)_4$) were tested. Experimental results supported by molecular dynamics simulations showed the correlation between molecule-graphene adsorption energy and the amount of dispersed graphene sheets. Remarkably, the results obtained imply that the performance of pyrene-assisted UILPE is indirectly driven by the molecular dipoles, which are not important per se, but since they facilitate the adsorption of pyrenes on graphene sheets by promoting the lateral displacement of the solvent molecules intercalating between the graphene sheets and pyrene cores.

Significantly, many other examples of increasing the yields UILPE of graphite in water by exploiting pyrene-graphene π-π interactions have been reported. In 2011, Lee and co-workers[107] revealed that an aromatic amphiphile based on a conformationally flexible

aromatic segment including four pyrene moieties (PyHD), stabilizes graphene dispersions in water with the concentration of 1.5 mg mL^{-1}. In other works Shi,[114] Müllen,[96] and Honma[106] used pyrenebutyrate (PyBA) and/or pyrenesulfonic acid (Py-SAH) to stabilize graphene in water for use in electrochemical, solar cell, and composite applications.

Recently, Liu and co-workers[115] designed naphthalene diimide (NDI) with ionic groups attached to the NDI unit through flexible alkyl spacers (see NDICA in Figure 2) and successfully used it as DSAs. It was demonstrated that NDICA exhibits an excellent capability to exfoliate graphite and disperse graphene in an aqueous solution, as revealed by the few-layered graphene concentration as high as 5 mg mL^{-1} after centrifuging at 1000 rpm or 1.2 mg mL^{-1} after centrifuging at 5000 rpm. The superior performance of the NDICA is ascribed to their chemical structures, which guarantee strong π-π interactions between the molecules and graphene and electrostatic (ionic) interactions between carboxylic groups of NDICA and water molecules.

Several perylene-based DSAs have been used to leverage the exfoliation of graphite in aqueous solutions, including sophisticated perylene diimide (PDI)-based bolaamphiphiles[94] (PDIBBA; Figure 4) and PDI-sulfonic acid ($PDI(SO_3)_2$).[96] An efficient method for the preparation of graphene by UILPE in aqueous dispersions, was reported by Stupp, Stoddart and co-workers,[116] where N,N'-dimthyl-2,9-diazaperopyrenuim dichloride (PDAP; see Figure 2) molecules were employed to stabilize dispersed graphene sheets in water. Nevertheless, the AFM study of the exfoliated material showed that the exfoliated graphene sheets are primarily 2 to 4 layers thick.

Because of the good performance of pyrenes, NIDs and PDIs as DSAs, other PAHs are also expected to stabilized graphene produced through UILPE of graphite. Some recent

examples revealed that both anthracene,[93] and coronene[95] can be used as DSAs. In particular, Lee and co-workers proved that the exfoliation of graphite can be also achieved by non-covalent functionalization using 9-anthracene carboxylic acid (ACA).[93] Amazingly, ACA-graphene based composites exhibit unique electronic properties, i.e. they hold high specific capacitance value of 148 F g^{-1}, as demonstrated by performance of ACA-graphene based ultracapacitor.

Over the past years, it has been shown that graphene can be dispersed in water by using various organic polymers as DSAs, [12, 89, 91, 92, 110, 111, 112, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126] like cellulose acetate (CA),[127] ethyl cellulose (EC),[123] polyvinylpyrrolidone (PVP),[118] lignin,[124] gum arabic (GA),[119, 120] gelatin derived from animal skin and bones,[121] and even more complex systems such as bovine serum albumin (BSA),[117] hyaluronan (PyHA)[111] and DNA[92] functionalized with pyrene units.

While majority of DSAs employed in UILPE of graphite have ionic nature, in their pioneering work Guardia and co-workers,[122] studied numerous nonionic DSAs, and compared them with their ionic analogues. It was concluded that the non-ionic DSAs significantly outperform their ionic counterparts. The best result, a graphene dispersion of ~1 mg mL^{-1}, was attained when the triblock copolymer Pluronic® P-123 (see Figure 3) was employed. AFM analysis showed that graphene sheets produced in presence of P-123 had lateral sizes in the range of hundreds of nanometers, and almost all the sheets were thinner than 5 layers thick (ca. 15% SLG), in accordance with other investigations of DSAs-assisted UILPE.

Figure 3. HERE

More recently, Farris and co-workers performed UILPE of graphite in water with the assistance of three polysaccharides, namely nonionic pullulan, cationic chitosan, and anionic alginate.[126] The effects of polymer type, initial concentration of graphite, and ultrasonication time on the graphene concentration and quality were benchmarked. Upon ultrasonication treatment for 30 min, graphene dispersions with concentrations of up to 2.3 mg mL^{-1} in pullulan-stabilized dispersions and 5.5 mg mL^{-1} in the case of chitosan were produced. The obtained graphene sheets were characterized as low-defect SLG, and FLG (<5). Findings arising from these studies suggest that pullulan and chitosan are outperforming alginate as DSAs, because of the different surface free energy and thermodynamic affinity.

The use of polymers as DSAs in the UILPE process is unquestionably more beneficial (from graphene dispersion concentration point of view) than the use of organic molecules, however because of the strong polymer/graphene interactions the majority of graphene produced by making use of this approach cannot be fully separated from polymer/graphene composites.

Interestingly, in some cases the elimination of the polymeric DSAs is not compulsory, and in fact their presence can have some benefits. In particular, Yoon and co-workers revealed that graphene dispersions can be stabilized by four different polymers based on either poly(vinyl alcohol) (PVA) or dextran functionalized with conjugated moieties, like phenyl or pyrene (see PyDT and PyPVA in Figure 3).[112] The ability of these polymers to stabilize graphene dispersions was systematically explored. Moreover, graphene hydrogels and aerogels were prepared from the aqueous dispersion of the graphene/polymer. The cross-linking of the dispersed polymers in the solution gave hydrogels with embedded graphene flakes inside the polymeric networks, and the subsequent freeze-drying of the hydrogel resulted in an aerogel. Compared with a control experiment on a PVA gel electrolyte (84.2 ± 5.2 F g^{-1}), the use of graphene/polymer gel electrolyte (107.5 ± 3.1 F g^{-1}) allowed higher specific capacitances and long-term cycling stability, which was attributed to the fact that

graphene embedded into the gel enhances the ionic conductivity of the gel.[128] These results clearly evidence the variety of possible applications for graphene/DSAs composites.

Despite the few aforementioned examples, residuals of the PAHs and polymeric DSAs, can utterly affect the electrical performance of graphene-based devices. Therefore, the search of inexpensive DSAs that have high stabilization efficiency, which can be easily removed has gathered a great attention in the field,[90, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138] as it will largely simplify the industrialization and application of graphene produced in aqueous dispersions.

Various examples of small DSAs an be found in literature (see Figure 4), including urea (U),[134] sodium salt of flavin mononucleotide (FMNS),[129] 1H,1H,11H-eycosofluor-1-decanol polyglycidyl ether (FAPGE),[136] amphiphilic compound consisting of alternating phenylene and thienylene subunits (PTPTP),[135] and (1,3,5-tris[(1E)-2'-(4'-benzoic acid)vinyl]benzene) (Ramizol®).[138] Lately, Palermo and co-workers[137] described the UILPE, processing and inclusion in polymer composites of FLG by using indanthrone blue sulphonic acid sodium salt (IBS), a very common industrial dye, and showed that IBS can be used to stabilize FLG dispersions in water. To establish that their method is suitable for applications in composites, graphene/IBS hybrids were processed into PVA, increasing its electrical conductivity by several orders of magnitude.

Figure 4. HERE

In 2014 Chen and co-workers described the UILPE of graphite in water into SLG and FLG sheets *via* the direct exfoliation of highly oriented pyrolitic graphite (HOPG) using pyridine (P) as DSA.[131] Electrical conductivity >5100 S cm^{-1} was observed for filtered graphene paper, and the exfoliated graphene exhibited superior performance as a hole

transport layer (HTL) compared to the commercial HTL, namely N,N-di(naphthalene-1-yl)-N,N-diphenylbenzidine (NBP), in a basic organic light-emitting diode (OLED) using tris-8-hydro- xyquinolinealuminum (Alq_3) as the emissive layer.

The same group has also reported on another DSA, namely imidazole,[130] which interacts with the exfoliated graphene sheets, dramatically improves the concentration of graphene dispersion (1 mg mL^{-1}) in water. Graphene film prepared from the exfoliated material revealed an electrical conductivity of 131.7 S cm^{-1}. Furthermore, an all-solid-state supercapacitor with a new design fabricated using the exfoliated graphene sheets delivered an ultrahigh area capacitance (~72 mF/cm^2).

Recently, Francis and co-workers demonstrated fine patterning of graphene by screen printing using a silicon stencil and a high conductivity ink based on graphene dispersions prepared by ethyl cellulose (EC) assisted UILPE in ethanol.[139] The screen-printed graphene patterns on polyimide films showed high electrical conductivity of 1.86×10^4 S m^{-1} and remarkable mechanical flexibility, suitable for electronic applications.

Regardless of the exfoliation yields and the stability of graphene aqueous dispersions, the use of water as an exfoliation media is not recommended for the exploitation of graphene in electronic devices such as field-effect transistors (FETs). In particular, the presence of water remaining at the interface with dielectrics can augment the occurrence of charge-trapping phenomena.[140] Therefore, the use of DSAs-assisted UILPE in organic solvents has to be explored.

2.2. Graphene dispersions in organic solvents

Despite the increasing interest in the field, the knowledge gathered about the DSA-assisted UILPE of graphite in organic solvents is still relatively poor.[123, 127, 141, 142, 143, 144, 145, 146, 147] The first reported example, dealing with this approach involves the use of

1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy(polyethyleneglycol)-5000] (DSPE-mPEG; Figure 5) molecules in a combination with TBA-inserted oleum-intercalated graphite.[144] Such mixture was sonicated in DMF to give homogeneous graphene dispersion, which was further deposited on various transparent substrates, including glass and quartz, by exploiting Langmuir-Blodgett (LB). The one-, two- and three-layer LB films on quartz afforded sheet resistances of 150, 20 and 8 $k\Omega\ sq^{-1}$ and transparencies of 93, 88 and 83%, respectively.

Figure 5. HERE

Porphyrins are known to interact with various carbon-based materials, such as graphite, CNTs and fullerenes through π-stacking that takes place between porphyrinic electron–abundant aromatic cores and conjugated surfaces.[148, 149, 150, 151] Therefore, similar interactions are expected to take place between porphyrins and graphene.[152, 153] To explore this idea, Jung and co-workers dispersed graphene in the presence of 5,10,15,20-tetraphenyl-(4,11-acetyltioundecyl-oxyphenyl)-21H,23H-porphin (TATPP; Figure 5) in NMP containing organic ammonium ions. It was found that the TATPP-assisted UILPE of graphite could be employed to produce SLG sheets with high quality.

Successful UILPE of graphite can be also attained in ethanol by exploiting a PEG terminated with a quinquethiophene moiety (5TN-PEG) as a DSA. The graphene films have been prepared *via* vacuum filtration, followed by removal of the 5TN-PEG molecules with THF and by chemical treatment with HNO_3 and $SOCl_2$. The graphene film displayed interesting opto-electronic performance (a transmittance of 74% at 550 nm, a sheet resistance of 0.3 $k\Omega\ sq^{-1}$ and $\sigma_{dc}/\sigma_{ac} = 3.65$).

Graphene directly exfoliated from graphite using UILPE and CTAB (see Fig. 5) as a DSA has been demonstrated by Valiyaveettil and co-workers.[146] The sheets could be

dispersed in common organic solvents like DMF. Characterization of the flakes by various techniques like TEM, AFM and SEM, revealed that the exfoliation into graphene flakes of average ~1.2 nm thicknesses. Field emission measurements exhibited a turn on voltage of 7.5 V μm^{-1} and emission current densities of 0.15 mA cm^{-2}.

The use of small organic molecules such as DSAs is expected to promote the UILPE of graphite when the DSA molecules have a strong affinity for graphene, especially being stronger than that of the solvent/graphene interactions. A good starting point can be the use of alkanes which are known to possess a high affinity for the basal plane of graphite/graphene.[154] In this framework, we have recently demonstrated that arachidic acid (C19CA; Figure 5) and *n*-octylbenzene (NOTB) can be efficaciously used to harness the exfoliation of graphene in NMP.[141] Notably, the addition of the C19CA and/or NOTB does not affect the quality and structure of graphene, when compared to the use of NMP alone, providing evidence for the non-invasive nature of the process. Furthermore, the use of alkyl chain based DSAs lead to an enhancement of the percentage of SLG and bilayer graphene flakes. In particular, by using NOTB as DSA the amount of SLG increases by ca. 10 % and graphene concentration increases of 25%, with respect to graphene exfoliated in pure NMP. Conversely the use of C19CA resulted in slightly lower increase of percentage of SLG and 50% increase of the concentration.

We have also demonstrated that the performance of linear alkanes exposing a carboxylic acid head group as DSAs directly depends on the length of the alkane chain.[143] To this end, we explored five linear modules, i.e. hexanoic acid (C6CA), lauric acid (C12CA), stearic acid (C18CA), lignoceric acid (C24CA) and melissic acid (C30CA) (Figure 5), whose different adsorption energies on graphene and marked tendency to form tightly packed self-assembled monolayers on such a surface affected their performances as DSAs. Analysis of the carboxylic acid assisted UILPE showed that the concentration of graphene dispersions prepared in NMP, *o*-DCB and TCB increases linearly with the length of the alkyl tail.

The observed dependence of the UILPE yield with the length of the aliphatic chain has been interpreted by means of a thermodynamic model of molecular self-assembly on graphene. Our analysis shows that the shorter the aliphatic chain, the larger the (rotational and translational) entropic cost of forming a 2D structure will be. These results suggest that a model based on molecular mechanics for the energetics and a statistical mechanic treatment of entropy, could be used to predict the efficiency of supramolecular building blocks as DSAs and guide the chemical design of the next generation of DSAs. Nevertheless, a contribution played by kinetics cannot be fully ruled out.

Besides the above examples on the use of simple DSAs in organic solvents, only a limited number of polymers has been exploited in the past years. In particular, through a modelling study, the group of Coleman have predicted that maximal graphene concentration can be attained when the polymer and solvent exhibit similar Hildebrand solubility parameters as the graphene sheets.[127] Albeit being effective, the graphene concentration in the dispersions obtained therein was unfortunately often very low; e.g., 0.141 mg mL^{-1} in cyclohexanone or 0.02 mg mL^{-1} in THF. The search for a suitable polymers acting as DSAs in conventional low-polarity, low-boiling-point organic solvents organic solvents is thus important to render highly concentrated graphene dispersions of high quality.

It has been demonstrated recently, that the exfoliated graphene in NMP can be stabilized with an acidic solution of the poly(isoprene-*b*-acrylic acid) (PI-*b*-PAA) or poly[styrene-*b*-(2-vinylpyridine)] (PS-*b*-P2VP) block copolymers[91] (Figure 3). Unfortunately, the thickness of graphitic flakes amounts to 44 and 2.5 nm, respectively, implying that the PI-*b*-PAA- and/or PS-*b*-P2VP-assisted UILPE protocol requires further optimization.

3. Conclusion

Ultrasound-induced liquid-phase exfoliation of bulk graphite is a particularly mild, versatile and potentially up-scalable approach to generate high-quality graphene inks using cheap tools available in all the labs. When exploited in the liquid phase, the supramolecular approach can be exploited to leverage the performance of ultrasound-induced liquid-phase exfoliation of bulk graphite. UILPE in the presence of a given solvent molecule with the aid of an additional molecule acting as an DSA is a route not only to circumvent graphene re-aggregation due to van der Waals attraction, but also to enhance the efficiency of exfoliation, thereby compromising the effort made during exfoliation. Moreover, the presence of the DSAs interacting with the graphene through non-covalent forces can be exploited to modulate the properties of the graphene by conferring novel functions to the 2D material. UILPE approach is extremely interesting from technological point of view as many applications rely on large-scale mass production using low-cost methods such as ink-jet and screen-printing or R2R. UILPE is attractive for the preparation of stable graphene inks that can be processed in thin conductive films and composites. A great deal of effort has been devoted to enhance the degree and the yield of UILPE of graphene. Yet, the yield of SLG sheets is still moderately low and requires long treatment with ultrasound. Additionally, the exfoliated material has quite an amount of graphitic waste, which adds another (purification) step into the UILPE process. In order to harness the yield and reduce the by-products, various alternative methods are being intensively investigated. Amongst the LPE approaches electrochemical exfoliation (ELPE) emerged in the last years as the most promising tactic to disperse graphene in liquid media.[48] Differently from UILPE, ELPE may cause the edge-oxidation of graphene flakes; nonetheless, the level of oxidation is still markedly lower than that of rGO, guaranteeing interesting opto-electronic properties to the materials. Moreover, the concentration of dispersion produced by ELPE can be as high as 50 mg mL^{-1}, being two orders of magnitude greater than the average concentration of UILPE dispersions.

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LEGENDS OF FIGURES

Figure 1. Schematic representation of the ultrasound-induced liquid-phase exfoliation (UILPE) process of graphite in the absence and presence of dispersion stabilizing agents (DSAs). Reproduced from Ref. [43] with permission from The Royal Society of Chemistry.

Figure 2. Chemical structure of functionalized polycyclic aromatic hydrocarbons (PAHs) used as dispersion stabilizing agents (DSAs) in the ultrasound induced liquid-phase exfoliations (UILPE) process, with their acronyms as used in the text.

Figure 3. Chemical structure of polymeric DSAs used in the UILPE process, with their acronyms as used in the text.

Figure 4. Chemical structure of small organic DSAs used in the UILPE process in water, with their acronyms as used in the text.

Figure 5. Chemical structures of organic molecules used as DSAs in the process of UILPE of graphite towards graphene in organic solvents, with their acronyms as used in the text.